

PATENT SPECIFICATION

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(19)



(54) PLATING PROCESS FOR CHROME

(71) We, VINTAGE CURACAO N.V. a body corporate of the Netherlands Antilles, of Kerkstraat 10 A, Willemstad, Curacao, Netherlands Antilles, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to chromium plating and provides novel chromium plated articles.

Our copending patent applications Nos; 2218/75 (Serial No. 1,492,702), 2219/75 (Serial No. 1,500,971), and 2221/75 (Serial No. 1,500,972) describe various electroplating solutions for depositing chrome on conductive substrates and the remarkable properties which may be achieved using these solutions under specified conditions of temperature and current density. Further investigation of the coatings using in particular an Auger spectrograph, a "Stereoscan" electron microscope and a million volt transmission electron microscope, has shown the formation of a new and distinctive form of bond between the chrome and the substrate. It is postulated that the additives described in our earlier patent applications permit higher current densities to be used without passivation taking place and that these higher current densities provide sufficient energy for the formation of the new type of bond. This bond is molecular in the sense that the interatomic bonds are directional rather than non-directional as in the case of metallic bonds. Analysis of the interfacial layer of a chrome deposit on spectrographically pure iron has shown the presence of carbon in a form analogous to carbide and also sulphur as will hereinafter be described. Whether the carbon and sulphur are essential to the improved properties or whether they are incidental is not yet fully clear, but the indications are that they are essential and that they come from the carboxylic acid additives and the sulphate in the bath respectively (this is shown by experiments on pure iron).

Briefly, the invention provides a chromium-plated substrate in which the chrome casting is bonded to the substrate by a molecular bond and carbide is present at the interface.

In the case of matt coatings the surface of the chrome is nodular and it has generally been observed that the chrome layer consists of columns comprising very fine crystals. This is in contrast to the conventional chrome coatings which form stratified cracked layers. The presence of the columnar structure suggests the presence of crystal nuclei at the interface which are built upon as deposition proceeds, sideways expansion being of course inhibited by neighbouring columns.

A number of tests have been carried out with an Auger spectrograph which is an apparatus for analysing the surface (i.e. the first two or three atomic layers) of a specimen. The specimen is placed in a high vacuum chamber and bombarded with argon ions. These ions gradually strip the surface of the specimen and the surface can be analysed in a non-contaminated chamber at any stage. The analysis involves exciting electrons in the surface atoms by electron bombardment so that they move from one orbit to another and measuring the energies of the Auger electrons emitted when the atoms return to their ground state. As the transmission of the Auger electron through the uppermost atoms is restricted, an accurate analysis of the surface layer can be achieved.

Figure 1 shows an Auger spectrograph trace of an interface of a chrome coating according to the invention deposited by using a preliminary reverse etch and strike technique on a stainless steel substrate. The characteristic features are carbon and sulphur peaks, the carbon peak being characteristic of carbon in carbide form. It is therefore believed that carbon and possibly sulphur form part of the molecular bond. Similar traces were found for

all coated stainless steel samples. A sample of uncoated spectrographically pure iron was similarly treated in an Auger spectrograph and no carbon or sulphur peaks were observed. A further sample of spectrographically pure iron was coated according to the invention again using a preliminary reverse etch and strike technique and a carbon peak and a small sulphur peak were observed. Traces from this second sample are shown in Figure 2. Traces 2 and 3 (the right and left hand traces respectively) correspond to different areas of the surface which have been stripped to slightly different extents and their differences show the sensitivity of the technique. Trace 2 shows no iron but shows chromium, carbon and argon. Trace 3 shows chromium, argon and iron (indicating that a deeper etch has been obtained) but also chlorine and sulphur. The chlorine and carbon must come from the carboxylic acid additive and the sulphur must come from the sulphate in the bath. Significantly there is no oxygen present so sulphur is not present as sulphate ion. The two traces also suggest (though this is by no means conclusive) that the carbon extends upwards into the chrome layer but that the sulphur is confined to a very narrow band.

The "Stereoscan" microscope is in many ways similar to a closed circuit television system in which the specimen is inside the camera. An advantage over an optical system is a much greater depth of focus.

Figure 3 of the drawing shows a Stereoscan photograph at a magnification of 220 of a coating according to the invention which has been etched with argon ions in an Auger spectrograph. The coating has not been completely removed but it is believed that the argon bombardment has stressed the coating causing it to crack and that the softer substrate has been etched away where it is exposed along the cracks. There is no sign whatever of curling of the coating at the cracks which suggests firm adherence to the substrate.

Figure 4 shows the unetched surface of a coating according to the invention in a Stereoscan photograph at a magnification of 10,000; the nodular surface formed by the ends of the crystal columns is clearly seen, the columns having a centre-to-centre spacing of about 3μ .

Figure 5 is a Stereoscan photograph at a magnification of 2,200 of a coating according to the invention stripped down to the interface in an Auger spectrograph using an argon beam normal to the surface. It shows a characteristic pyramidal structure, with the spacing of the pyramids again being about 3μ . The pyramids are similar to those observed with similar experiments on uncoated steels containing hard carbides of the titanium or vanadium type.

Figure 6 is similar to Figure 5 but at a magnification of 11,500.

Figure 7 is a view similar to Figure 5 at a magnification of 195 and showing a surface of a similar specimen stripped by an argon beam incident at a shallow angle to the surface. The slant of the pyramids corresponds to the direction of the argon beam and again suggests the presence of hard nuclei at the interface.

Experiments were also carried out with a million volt electron microscope. A specimen coated according to the invention was further coated with a transparent lacquer and chemically etched from the rear until an aperture was formed. The edge of this aperture was examined with the electron microscope at 900 kV and Figures 8 to 12 show the experimental results obtained:-

Figure 8 - Magnification 640; shows serrated edge due to the machined surface of original specimen and preferential plating at the edges of the machining marks.

Figure 9 - Magnification 6,300; as Figure 8 at higher magnification.

Figure 10 - Magnification 18,900; as Figure 9 at higher magnification.

Figure 11 - Magnification 10,000; bright field view of the specimen (i.e. using central objective aperture).

Figure 12 - Magnification 29,000; shows a Bragg ring obtained from the crystals of Figure 11.

Figure 13 - As Figure 11 but a dark field view (i.e. only electrons diffracted in a particular direction are picked up). The alignment of the bright parts of this photograph suggests that there is a particular crystal orientation round the columns.

The hardness of the coatings according to the invention is due to the bond at the interface and to some extent the fine crystal structure in the columnar form. In fact the hardness decreases as more chrome is applied to the substrate.

Because of the thin coatings involved e.g. 10μ , the standard Vickers test is modified to use a reduced load of 30 gm but the size of the indentation is measured in the normal way and the necessary weight correction made. Vickers hardness of up to 1500 may be readily and regularly achieved whereas prior chrome coatings could only achieve a Vickers hardness of 1000 and then only with great difficulty. It is believed that the hardness is due to the formation of very small random crystals at the interface, the possibility of crystal dislocation there, and the pinning of these dislocations.

The adhesion of the coatings according to the invention has already been referred to, and this property is fundamental to their advantageous properties. Conventional hard chrome

coatings are brittle and when applied to machine tools break up and flake away from the substrate after a short period of use. Coatings according to the invention on the other hand have excellent adherence and can give machine tools a hard, longlasting surface. Experiments have shown that when coatings according to the invention are forcibly stripped for the substrate, they carry part of the substrate with them, their adhesion to the substrate being greater than the cohesion of the substrate, e.g. as shown in Figure 14.

The lubricating properties of the nodular surface have been referred to above. In general properties of the coatings can be varied between hard and ductile and between bright and matt. For machine tool applications the coatings will normally be hard matt coatings on tool steel. Experiments have shown that the life of machine tools can be increased nine or more times using coatings according to the invention. However, ferrous metal substrates are not the only substrates which can be used; coatings on aluminium and brass for example have been successful.

Preferred chrome coatings of the invention have one or more of the following features:-

- (a) their adhesion to the substrate is such that when forcibly removed they remove part of the substrate with them.
- (b) their adhesion is such that when stripped in an Auger spectrograph until they crack, no curling of the edges of the cracks can be observed.
- (c) their hardness is at least 1050 Vickers, preferably at least 1100.
- (d) their hardness decreases as their thickness increases.
- (e) they have a columnar structure generally with a centre-to-centre spacing of 2-4 μ .
- (f) they have a nodular surface structure generally with a centre-to-centre spacing of 2-4 μ .
- (g) when stripped in an Auger spectrograph by argon bombardment they display pyramids generally with a centre-to-centre spacing of 2-4 μ .
- (h) the Auger spectrograph trace at the interface shows the presence of carbon and/or sulphur.
- (i) the coefficient of friction is substantially reduced particularly the coefficient of static friction between two surfaces according to the invention is less than 0.18 preferably less than 0.16.
- (j) the corrosion resistance of mild steel provided with a 5 μ coating according to the invention satisfies and passes the standard salt spray test used in the British motor industry.

The method for obtaining coatings according to the invention is described in the copending patent applications mentioned above, the contents of which are incorporated herein by reference. Some of the methods of obtaining coatings according to the invention will, however, be now described for the sake of completeness.

The bath used normally contains a hexavalent chromium as chromium trioxide preferably in a concentration of 200 to 600 g/l, particularly in a concentration of 200 to 550 g/l. The bath may contain 1 to 18 g/l strontium sulphate and 2 to 30 g/l potassium silicofluoride which are conventional additives. Potassium dichromate is also a conventional additive which may be included, e.g. at a concentration of 2 to 8 g/l, although the purity of the other ingredients now available makes it less important than it previously was. The bath also contains 4 to 50 g/l of technical 2,2-dichloromalonic acid or a salt thereof. By technical dichloromalonic acid, we mean that the ratio of monochloromalonic acid or monochloromalonic salt thereof to the dichloromalonic acid or salt thereof is less than 1:10 and preferably less than 1:19. Typical bath compositions are set out in the following examples:

Example 1

50	Electrolyte consisting of:	405	g/l chromium trioxide	50
		15	g/l potassium silicofluoride	
		7.5	g/l strontium sulfate	
		7.5	g/l 2,2-dichloromalonic acid	

Example 2

55	Electrolyte consisting of:	382	g/l chromium trioxide	55
		3.8	g/l potassium silicofluoride	
		7.2	g/l strontium sulfate	
60		32.0	g/l 2,2-dichloromalonic acid	60
		6.5	g/l potassium dichromate	

Current densities of 40 to 500 amp/dm², particularly 50 to 200 amp/dm², may be used. Temperatures may, for example, be 45 to 60°C particularly 53 \pm 2°.

The ratios of 2,2-dichloromalonic acid to strontium sulfate and, on the other hand, of

2,2-dichloromalonic acid to potassium silicofluoride have well determined effects on the properties of the coating. The electrolyte may be varied according to the desired results.

It has been ascertained that, with unchanged amounts of 2,2-dichloromalonic acid and sulfate but with an increased amount of potassium silicofluoride (between 2 g/l and 20 g/l), an increase of up to 20% of dispersion of the coating is obtained with a loss of up to 100 Vickers hardness units.

With unchanged amounts of 2,2-dichloromalonic acid and potassium silicofluoride but with an increased amount of 1 to 10 g/l of sulfate one gains an increase in hardness of the coating up to 1500 Vickers units, with simultaneous reduction of the elasticity of the coating.

On the other hand, if the amount of 2,2-dichloromalonic acid is increased from 4 to 35 g/l, the conductivity of the bath will be improved with an increase in the current efficiency. By increasing the amount of 2,2-dichloromalonic acid to more than 50 g/l one obtains hard-brittle chromium coatings. A possible shortage of potassium may be replenished by inorganic and/or organic potassium salts, e.g. potassium dichromate.

An electrolyte composition as cited in Example 1, is suitable for depositing wear-resistant chromium coatings because their hardness, at a favourable bath temperature of 51 to 55°C, can be adjusted from 1200 to 1500 Vickers units using 50 to 200 amp/dm² current density. The resulting reduction of the coating elasticity will thereby increase the formation of cracks.

An electrolyte composition as cited in Example 2, produces more ductile chromium coatings which are well suited for lengthening the life of cutting tools. At a favourable bath temperature of 51 to 55°C the hardness of the coating may be adjusted from 1050 to 1250 Vickers units using 50 to 200 amp/dm² current density. The formation of cracks is thereby correspondingly low (of the order of 10 cracks/cm).

The chromium plating bath according to the invention allows an increase of the deposition rate of the chromium coatings, as follows:-

- 0.5 μ/minute at a current density of 50 amp/dm²
- 1.2 μ/minute at a current density of 130 amp/dm²
- 1.5 μ/minute at a current density of 200 amp/dm²

The increase in coating thickness does not show a linear relationship with an increase in current density.

The quality of the chromium coating can also be influenced, as known from other chromium baths, through variation of the bath temperature. With increased bath temperature the dispersion capacity and hardness decline. With lowered bath temperature the dispersion capacity as well as the hardness will be slightly improved. Chromium coatings which have been deposited at an electrolyte temperature of less than 45°C are hardly ever applied technically. The temperature in Examples 1 and 2, is 53° ± 2°C.

The pearloid structure of the chromium coatings according to the invention which depends exclusively on the surface quality of the substrate and the current density, shows very favourable anti-frictional properties. The following comparisons illustrate the coefficients of friction of various metals with a chromium coating according to Example 2.

Materials	Coefficient of friction	
	Static	Dynamic
steel against steel	0.21	0.15
steel against chrome	0.18	0.13
chrome against chrome	0.14	0.11

The good adhesive capacity of the chromium coatings can be proved experimentally as follows:-

A bending rod of 2 mm ø covered with a chromium coating according to the invention of 5 - 10μ, when bent over a radius of 10 mm, shows cracks only after a bending of 18°. With a bending of 180° the cracks extend to the substrate. However, no chromium particles will break away as is normally the case with chromium coatings.

For good adhesion of chromium coatings to the substrate, pretreatment of the latter is necessary. It is important to remove the very thin oxide film which adheres to every metal, and to prevent the forming of a new film before the workpiece is placed in the bath. The best results are obtained by using aqueous jets, containing glassmeal, wherein an inhibitor e.g. 0.5% NaNO₂ (sodium nitrite) is added to the water.

Hydrogen embrittlement of the workpiece is less prevalent in the baths used for the invention than in previously known baths. The duration of exposure of the workpiece to be treated is, by reason of the rapid deposition of the coating which can be up to 1.5μ/min. and the relatively thin chromium coating of 5 - 10μ, very short. Any iron-chromium carbide

formation which takes place as well as the deposition of chromium and the Joulean heating are highly energy absorbing so that relatively less energy remains available for the dissociation of hydrogen. The hydrogen, which is formed from the electrolyte re-combines partially with the dissociated oxygen to form water, on the surface of the workpiece (point of energy transformation), the rest volatilizing. To discharge the remaining hydrogen, which penetrates into the workpiece, it is known to apply heat treatment after a chromeplating process, whereby through the effects of heat at 200°C for 4 hours, approximately 80% of hydrogen can be expelled. This post-treatment is recommended with workpieces which are highly carbonaceous and especially thin-walled, e.g. knife edges, springs and the like. It is thereby pre-supposed that steels with a low carbon ratio and those with more than 1.5% silicon or those which have been tempered at higher ranges of temperature are less sensitive to diffusion of hydrogen.

Another factor reducing hydrogen embrittlement is vigorous circulation of the electrolyte which must take place during the plating process. The dissociated hydrogen is thereby rapidly removed from the workpiece. Furthermore, the vigorous agitation of the electrolyte, circulated about 8 times the bath content per hour, causes maximum solubility of the chemical components contained in the bath. In the bath itself there is no formation of bottom sediment as it occurs with known SRHS (self regulating high speed) baths. The quality of the electrolyte therefore remains at an optimum for lengthened periods of use. The electrolytes according to Examples 1 and 2 are suitable for the deposition of chromium coating on all materials known to be chrome-plateable; they are therefore not dependent on the substrate. The cleanliness of the substrate may be ensured by such standard procedures as degreasing with a solvent, vapour-blasting, pickling cathodic or anodic cleaning (the former for non-ferrous materials and the later for ferrous materials) and rinsing in de-ionized water. It is also desirable to heat the substrate to the plating temperature before immersion in the plating tank.

For ferrous metal substrates, a reverse etch step in the plating tank is advantageous. In other words the polarity of the voltage is reversed briefly according to standard procedures before the plating process begins. It is also advantageous to include a "strike" step in which the current density is increased by say 50 to 100% for a very brief period at the beginning of plating.

Our compending patent application No. 2218/75 (Serial No. 1 492 702) describes and claims a workpiece which has been chromium-plated by a method for the electrodeposition of a chromium coating on a substrate wherein deposition is effected from a bath for the electrodeposition of chromium comprising an aqueous chromium (VI) solution containing 200 to 550 g/l chromium trioxide, 1 to 18 g/l strontium sulfate, 2 to 30 g/l potassium silicofluoride and 4 to 50 g/l 2,2-dichloromalononic acid or a salt thereof at a temperature in the range 45°C to 60° and a current density in the range 40 to 560 amp/dm², wherein the substrate is of a ferrous metal, and wherein through the formation of an iron-chromium carbide zone on the surface of the workpiece the binding of the chromium coating upon it is of molecular type. We make no claim herein to such a workpiece and subject to this disclaimer:

WHAT WE CLAIM IS:-

1. A chromium-plated substrate in which the chrome coating is bonded to the substrate by a molecular bond and carbide is present at the interface.
2. A chromium-plated substrate according to claim 1 which is of ferrous metal.
3. A chromium-plated substrate according to claim 2 which is of steel.
4. A chromium-plated substrate according to any preceding claim in which the chrome coating has a hardness of at least 1050 Vickers units.
5. A chromium-plated substrate according to any one of claims 1 - 4 wherein an Auger spectrograph trace at the substrate-coating interface shows the presence of carbon and sulphur.
6. A chromium-plated substrate according to any one of claims 1 - 4 wherein the coefficient of static friction between the chrome-coating surface and a similar surface is less than 0.18.
7. A chromium-plated substrate according to claim 6 wherein the coefficient of friction is less than 0.16.
8. A chromium-plated substrate according to any preceding claim wherein the adhesion of the coating to the substrate is such that when it is forcibly removed, part of the substrate comes away with the coating.
9. A chromium-plated substrate according to any preceding claim wherein the adhesion of the coating to the substrate is such that when it is stripped in an Auger spectrograph until it cracks, no curling of the edges of the cracks can be observed.
10. A chromium-plated substrate according to any preceding claim wherein the hardness of the chrome coating decreases when further chrome is deposited.

11. A chromium-plated substrate according to any preceding claim wherein the coating has a columnar structure generally with a centre-to-centre spacing of $2-4\mu$.

12. A chromium-plated substrate according to any one of claims 1 to 10 wherein the coating has a nodular surface structure generally with a centre-to-centre spacing of $2-4\mu$.

5 13. A chromium-plated substrate according to any preceding claim which is such that when stripped in an Auger spectrograph by argon bombardment it displays pyramids generally with a centre-to-centre spacing of $2-4\mu$. 5

10 14. A chromium-plated substrate according to claim 1, substantially as hereinbefore described. 10

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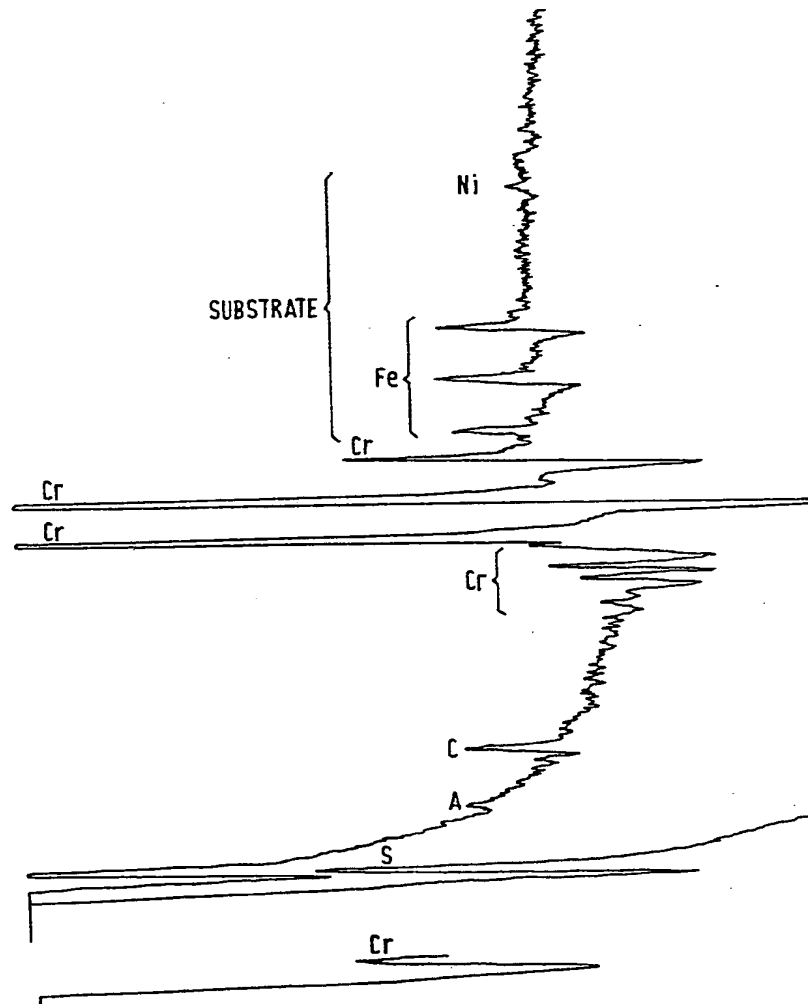


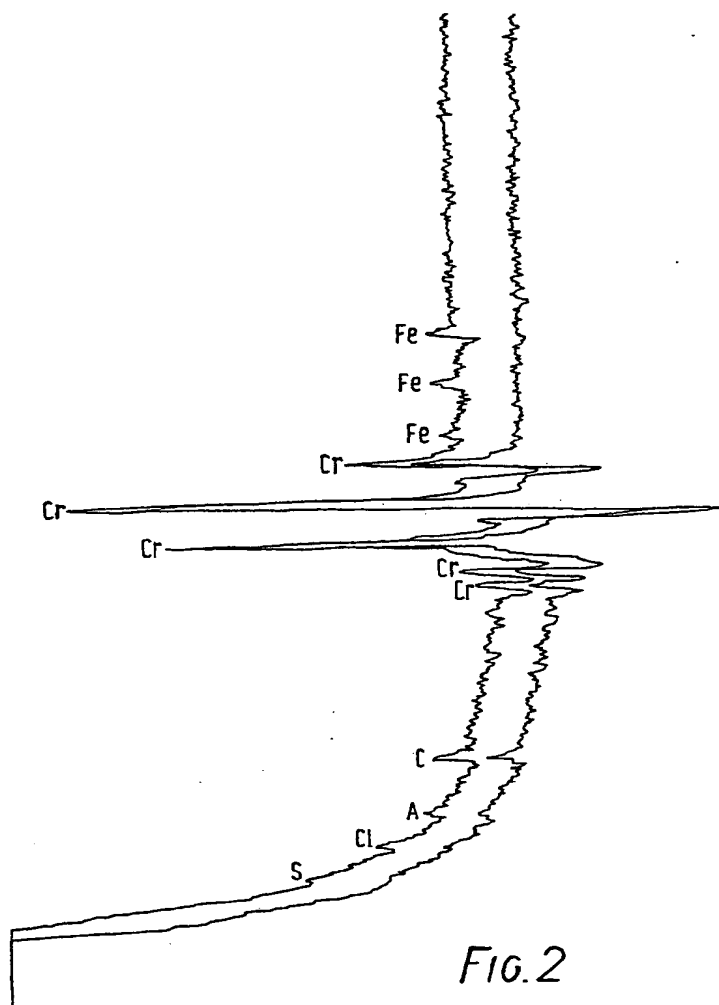
FIG. 1

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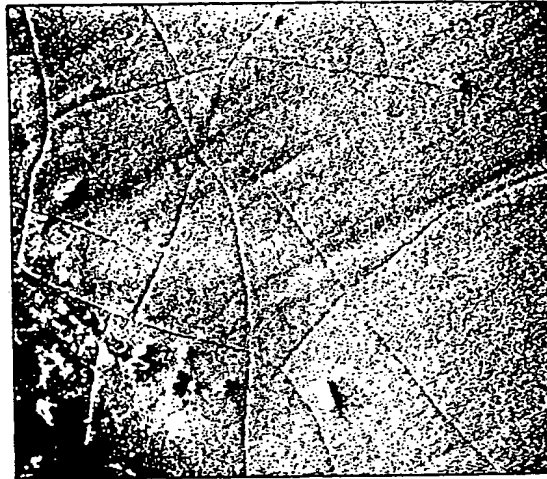


FIG.3

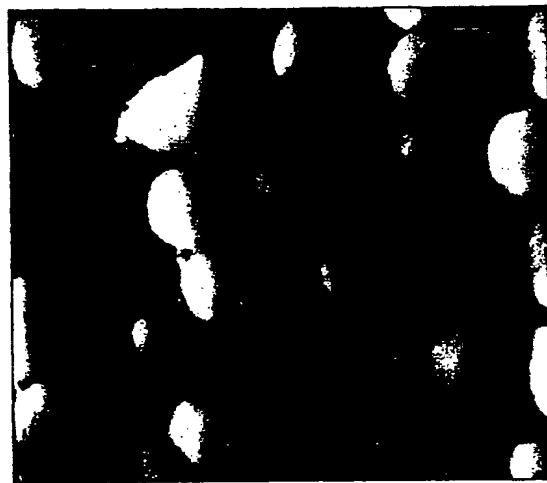


FIG.4

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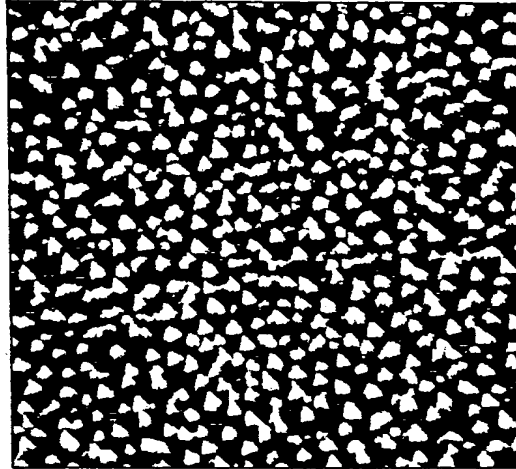


FIG. 5

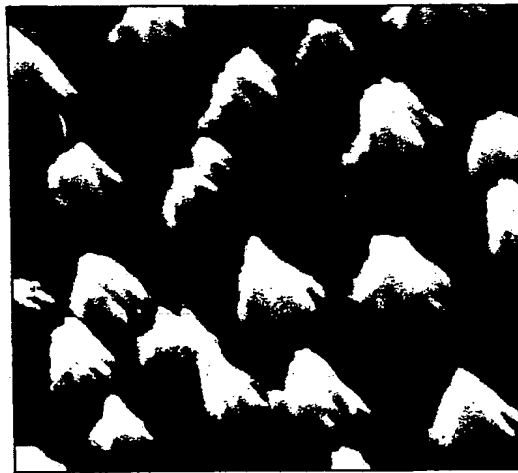


FIG. 6

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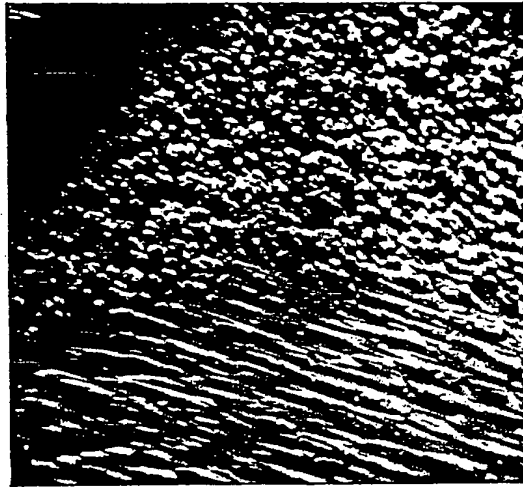


FIG. 7

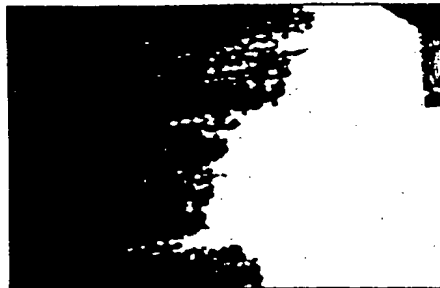


FIG. 8

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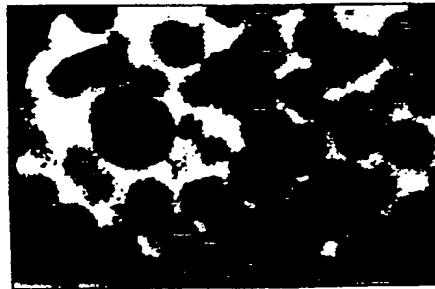


FIG. 9



FIG. 10



FIG. 11

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FIG. 12



FIG. 13

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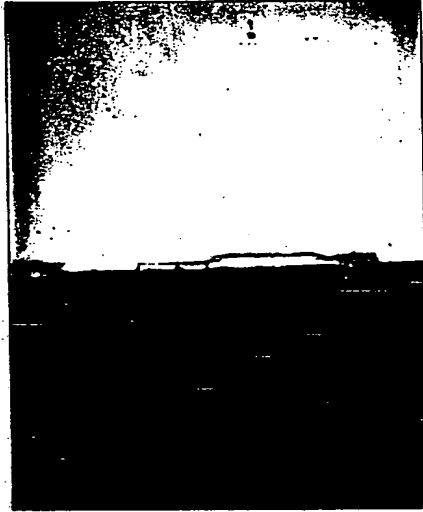


FIG. 14

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